LDEQ-EDMS Document 36717066, Page 2 of 16

STATE OF LOUISIANA

DEPARTMENT OF ENVIRONMENTAL QUALITY

IN THE MATTER OF: * Settlement Tracking No.

* SA-AE-06-0049

PRAXAIR, INC.

*

AI # 2218 * Enforcement Tracking No.

AE-CN-05-0200

PROCEEDINGS UNDER THE LOUISIANA ENVIRONMENTAL QUALITY ACT

LA. R.S. 30:2001, <u>ET SEQ.</u>

SETTLEMENT

The following Settlement is hereby agreed to between Praxair, Inc. ("Respondent") and the Department of Environmental Quality ("DEQ" or "the Department"), under authority granted by the Louisiana Environmental Quality Act, La. R.S. 30:2001, et seq. ("the Act").

Ι

Respondent is a corporation that operates a chemical production facility southeast of the intersection of Louisiana Highway 73 and River Road in Geismar, Ascension Parish, Louisiana ("the Facility").

II

On April 6, 2006, the Department issued to Respondent a Consolidated Compliance Order and Notice of Potential Penalty, Enforcement No. AE-CN-05-0200, which was based upon the following findings of fact:

The Respondent owns and/or operates a chemical production facility known as the Geismar Plant (the facility) located southeast of the intersection of Louisiana Highway 73 and River Road in Geismar, Ascension Parish, Louisiana. According to the Respondent in an August 11, 2003 letter, and a Change of Ownership form signed on April 7, 1997, by the Department acknowledging a

change in the facility's ownership, the facility was purchased from Liquid Carbonics, a wholly owned subsidiary of Chicago Bridge & Iron in January 1996. The facility currently operates under Title V Permit No. 0180-00031-V1 issued on July 18, 2003.

The Respondent submitted a letter dated August 24, 2005, detailing ammonia emissions from the Reformer Flue Gas Stack, Unit VI (Emission Point 9-95). Title V Permit No. 0180-00031-V1 requires in Part 70 Specific Condition No. 1 that emissions from Reformers I, II, III, IV, and VI at the Geismar Facility (Emission Points 1-71, 1-81, 2-88, 3-94, and 9-95) are limited to an emissions cap for particulate matter, sulfur dioxide, nitrogen oxides (NO_x), carbon monoxide, volatile organic compounds and ammonia. According to the August 24, 2005 letter, ammonia is emitted only from the Reformer Flue Gas Stack, Unit VI (Emission Point No. 9-95), which is controlled by selective catalytic reduction. In the letter, the Respondent reported that emissions were above the maximum permitted level for ammonia based on a 12 consecutive month period.

To demonstrate compliance with the Facility-Wide Averaging Plan (FWAP) approved by the Department on April 17, 2005, in accordance with LAC 33:III.2201.E.1 and LAC 33:III.2201.F.7, Reformer Flue Gas Stack, Unit VI was initially tested to demonstrate compliance with NO_x emission limits and other pollutant limits as applicable including ammonia in March 2005. As per LAC 33:III.2201.J.2, the deadline for initial demonstration of compliance was no later than November 1, 2005. According to the Respondent's letter dated August 24, 2005, the initial test results and report were reviewed in May 2005, and because the initial stack test results for ammonia were inconsistent with the manufacturer's information, Reformer Unit VI was to be retested in June 2005. According to the Respondent's August 24, 2005 letter, prior to this time, the permitted ammonia emissions from this reformer were based on data provided by the catalyst's manufacturer, which is listed in the Louisiana Air Permit Procedures Manual as an approved basis for allowable permitted emission

rates. In a notification letter dated May 31, 2005, the Respondent notified the Department of its intention to perform compliance emissions source testing of Reformer Unit VI for ammonia emissions beginning the week of June 20, 2005. The tests were conducted on or about June 20, 2005 through June 21, 2005, with the results again indicating emissions of ammonia in excess of the maximum pounds per hour permit limit.

The Respondent was granted an exemption to test on July 1, 2005, to perform an engineering study on Reformer Unit VI to verify Selective Catalytic Reduction (SCR) effectiveness.

The August 24, 2005 letter noted that because of the results of the two stack tests for the Reformer Unit VI, an engineering study was performed on or about July 6, 2005 through July 8, 2005, in order to verify the accuracy of the earlier stack tests. According to the Respondent's letter, as a result of this engineering study, the Respondent was able to operate Reformer Unit VI in a manner which limited the ammonia emissions to less than that of the manufacturer's data and in compliance with the permitted hourly limit. The Respondent explained in an unauthorized discharge report dated July 15, 2005, that to limit the ammonia emissions the ratio control for ammonia was readjusted. In addition, the Respondent noted in the July 15, 2005 report that the facility has a high ammonia flow alarm capability which limits the quantity of ammonia to ensure that no further unauthorized discharges of ammonia occur based on normal operation of the Reformer Unit VI.

According to the Respondent's letter dated August 24, 2005, due to the time period that the two separate stack tests and the engineering study were being conducted, and the ammonia emissions were determined to be greater than the manufacturer's data, the annual emission rate for ammonia, based on a 12 consecutive month period, exceeded the permitted amount for each consecutive 12 month period ending in the months of April through July of 2005. According to the Respondent, the

annual emission rate for ammonia, on a 12 consecutive month basis, will continue to exceed the permitted level for several months although the ammonia emissions from Reformer Unit VI were calibrated to bring the ammonia emissions into compliance with the hourly permitted limit.

On or about October 19, 2005, the Respondent met with representatives of the Department which included representatives of the Enforcement Division. The Respondent provided a timeline of the events that had transpired up until the date of the meeting. The Respondent was requested to submit the 12 consecutive month rolling total ammonia emissions data for the period of noncompliance for Reformer Unit VI.

In response to the meeting on or about October 19, 2005, the Respondent submitted ammonia emissions data for Reformer Unit VI which indicated that the 12 consecutive month rolling total had been exceeded beginning in April 2005. The data indicated that the ammonia emissions 12 consecutive month rolling totals were exceeded for each 12 consecutive month period ending in the months of April 2005, May 2005, June 2005, and July 2005.

The Respondent also submitted a Title V semiannual monitoring report dated September 23, 2005, which reported the ammonia exceedances as deviations in attached reports dated July 15, 2005, and August 24, 2005. In the report the Respondent included monthly emissions totals, as well as the 12 consecutive month totals for each month of the semiannual period. The 12 consecutive month totals for April 2005, May 2005, and June 2005, indicated exceedances of the ammonia emission Reformer Cap limit.

By letter dated October 27, 2005, the Respondent requested an extension of time for the initial compliance demonstration testing and continuous emissions monitoring system (CEMS) certification caused by the effects of Hurricanes Katrina and Rita on the Geismar facility, including setting up and removing the necessary scaffolding, making other arrangements for such tests, and subsequently having to cancel such tests (originally the stack tests were scheduled for September 6,

2005 but could not begin until October 10, 2005.) The Respondent noted in the request that the test was not successfully completed on October 10, 2005 because of technical questions being raised by the very nature of the testing process.

The Respondent was granted an extension by letter dated November 9, 2005, to determine the cause of the testing problems and to again conduct the required tests on Reformer Unit VI and certify its CEMS by January 31, 2006.

By letter dated November 30, 2005, the Respondent requested a further extension of the previous extension granted on November 9, 2005, for conducting the initial compliance demonstration testing on Reformer Unit VI and certification of its CEMS as provided in the Respondent's FWAP. The November 30, 2005 request was submitted after a meeting with representatives of the Respondent and representatives of the Department on November 18, 2005. According to the November 30, 2005 letter, when the Respondent submitted its October 27, 2005 letter requesting an extension, it had not yet concluded that the stack test problems for Reformer Unit VI were caused by the catalyst on the reformer losing effectiveness much sooner than the four (4) to five (5) years of useful life warranted by the manufacturer. According to the Respondent, the present catalyst on Reformer Unit VI was 2.5 years old and was not utilized outside of normal plant operations. The Respondent requested that the deadline for performing the initial compliance tests on Reformer Unit VI and certification of its CEMS be extended further past January 31, 2006. The Respondent noted that a plant turnaround, originally scheduled for January 2006, had to be rescheduled because of the dearth of necessary contractors to work at the Respondent's Geismar facility due to the after effects of Hurricanes Katrina and Rita. The Respondent's request noted that the turnaround had to be rescheduled for March 31, 2006 through April 28, 2006. The Respondent

requested that the catalyst be installed during the same time frame. The request noted that in this way, the new catalyst will be ordered and installed during the March 30, 2006 through April 28, 2006, plant turnaround and avoid a separate plant shutdown of ten (10) to fourteen (14) days to install the new catalyst.

The Respondent was granted a letter of no objection on December 13, 2005, to extend the date to April 30, 2006, to conduct the initial compliance test on Reformer Unit VI and its CEMS from the previous extension of January 31, 2006.

On or about January 5, 2006, a representative of the Respondent met with the Department to discuss the SCR catalyst on Reformer Unit VI at the Geismar facility. In the meeting it was discussed that the Respondent had discovered that the ammonia exceedances had occurred as a result of the catalyst losing its effectiveness earlier than what the manufacturer had guaranteed. The representative of the Respondent was asked to provide a letter documenting the cause of the ammonia exceedances for Reformer Unit VI to the Enforcement Division.

The Respondent submitted a letter dated January 27, 2006, which identified the cause of the ammonia exceedances for Reformer Unit VI. The Respondent noted in the letter that in consultation with the catalyst manufacturer, the Respondent had identified catalyst poisoning as the cause of its temporary ammonia exceedances. According to the Respondent, the causation was previously unknown to the Respondent and only recently discovered even by the very experienced catalyst manufacturer and recently verified by the manufacturer's tests in its Denmark facility as being applicable to the process at the Geismar facility. The Respondent noted that the catalyst manufacturer was just becoming aware of this effect on the Respondent's operations, especially after the manufacturer recently analyzed the prior catalyst removed in 2003 after only two (2) years of

operation. According to the Respondent's January 27, 2006 letter, the manufacturer recommended that the catalyst can be utilized for four to five years. According to the Respondent's letter, when the catalyst was examined by the manufacturer at its facilities in Denmark, it was found to be 76 percent deficient, apparently caused by chrome poisoning. The Respondent noted that the current catalyst and operation process is the same as that of the 2003 catalyst and operation; and it is its belief that it is reasonable to conclude that chromium poisoning was again taking place which was reflected in the series of stack tests and the engineering study conducted in 2005.

The Respondent noted in the January 27, 2006 letter that to now be able to monitor the amount of ammonia emissions, an additional NO_x analysis point will be added upstream of the SCR catalyst bed (a CEMS analyzer is downstream from the catalyst). The resulting measurement can be used to set ammonia feed rates and prevent excess ammonia emissions in the future. The Respondent explained in the letter that by knowing the amount of ammonia injected, comparing the NO_x measurement from each analyzer, and performing a mathematical calculation, the amount of ammonia will be able to be monitored.

The Respondent noted in the January 27, 2006 letter that Reformer Unit VI represents two-thirds of the Geismar facility's production of hydrogen and that the costs of a consultant and legal fees, purchase and installation of a new catalyst, and employee time in investigating and correcting the problem was well in excess of \$500,000.00. The Respondent also noted that there would be additional costs associated with the installation of an additional NO_x analysis point upstream of the catalyst bed and the installation of a \$250,000.00 catalyst every two (2) years instead of every four (4) to five (5) years as previously recommended by the catalyst manufacturer.

The Respondent again met with the Department on or about February 21, 2006. The

Respondent discussed the corrective actions for the ammonia exceedances which included the installation of an upstream NO_x analyzer and inquired as to the status of the Order which had been requested. The Department and the Respondent discussed the information that had been provided by the Respondent in an email sent on February 20, 2006. The February 20, 2006 email was in response to several questions that had been raised by the Department in an email sent on February 16, 2006. In response to the Department's email, concerning the question of how the ammonia feed rate had been adjusted in the past, the Respondent noted that the ammonia feed rate was based upon a calculated factor (determined by AP-42 for natural gas, purge gas and air preheat) which is operated by ratio control to the firing rate of the reformer. The Respondent explained that as production (firing) rate increases or decreases, the ammonia flow follows automatically. According to the Respondent, Reformer Unit VI utilizes a Foxboro DCS, and therefore, all process monitoring and control is computer controlled. The Department also asked in the email how often in the past, since Praxair owned the facility, had the catalyst been changed. The Respondent responded that since Praxair operated the facility in December 1996, and with the catalyst change to be performed in April 2006, there would have been four (4) change outs in ten (10) years. The Department also requested in the email, the vendor's guarantee for the catalyst installed in 2003. The Respondent noted that the vendor's guarantee for the catalyst installed in 2003 was identical to the catalyst installed in 2001, including the catalyst specifications, as provided in the January 27, 2006 letter.

On or about March 6, 2006, a file review of the Respondent's facility was performed to determine the degree of compliance with the Act and the Air Quality Regulations. The file review encompassed discussions with the Respondent at meetings and correspondences (including, but not limited to letters and email) and reports from the Respondent.

The following violation was noted during the course of the file review:

Based on the information supplied by the Respondent in letters, reports, and meetings, the Respondent exceeded the maximum pound per hour limitation for ammonia for the Emission Cap for the Reformers. In addition, the Respondent exceeded the 12 consecutive month rolling total ammonia emissions for the Emission Cap for the Reformers. Each exceedance of the maximum pound per hour permit limitation as listed on the Emissions Inventory Questionnaire (EIQ) for the Emission Cap for the Reformers for ammonia is a violation of Louisiana General Condition III of Title V Permit No. 0180-00031-V1 and LAC 33:III.501.C.4. Each exceedance of the 12 consecutive months rolling total ammonia limit is a violation of General Condition III as listed on the EIQ for the Emissions Cap for the Reformers, Part 70 Specific Condition No. 1 of Title V Permit No. 0180-00031-V1 and LAC 33:III.501.C.4. Each exceedance is also a violation of Sections 2057(A)(1) and 2057(A)(2) of the Act.

In a facsimile dated March 31, 2006, the Respondent provided the temporary written procedure that had been developed and implemented to ensure compliance with the permitted maximum pound per hour emissions limitation for ammonia. The Respondent noted in the facsimile that the SCR catalyst had been changed, and the ammonia injection grid had been inspected. Representatives of the Respondent stated in conversations on April 3, 2006, that certification of the CEMS for Reformer Unit VI required by the FWAP and LAC 33:III. Chapter 22 had been performed, and that stack testing will follow. The Respondent submitted correspondence by facsimile on April 3, 2006, indicating CEMS certification tests were conducted on December 20, 2005, through December 26, 2005, and January 18, 2006.

Ш

In response to the Consolidated Compliance Order and Notice of Potential Penalty, Respondent made a timely request for a hearing.

IV

Respondent denies it committed any violations or that it is liable for any fines, forfeitures and/or penalties.

Nonetheless, Respondent, without making any admission of liability under state or federal statute or regulation, agrees to pay, and the Department agrees to accept, a payment in the amount of THREE THOUSAND THREE HUNDRED FIFTY-SEVEN AND 95/100 DOLLARS (\$3,357.95) which represents DEQ's enforcement costs, in settlement of the claims set forth in this agreement. The total amount of any money expended by Respondent on penalty payments to DEQ as described above, shall be considered a civil penalty for tax purposes, as required by La. R.S. 30:2050.7(E)(1).

In addition, Respondent agrees to comply with the Order portion of the Consolidated Compliance Order and Notice of Potential Penalty which states that the upstream NO_x CEMS shall be maintained and kept operational to ensure that compliance is demonstrated with the ammonia emission limitations specified in Title V Permit No. 0180-00031-V1 issued on July 18, 2003. In addition to the requirements specified in Part 70 Specific Condition No. 1 of Title V Permit No. 0180-00031-V1, the Respondent shall use the data from the upstream NO_x CEMS, the data from the downstream NO_x CEMS (downstream of the SCR catalyst bed), and the amount of ammonia injected to calculate the ammonia emissions monthly just as the required calculation frequency required by Part 70 Specific Condition No. 1 of Title V Permit No. 0180-00031-V1. The Respondent shall continue to comply with the recordkeeping and reporting requirements as specified in Part 70 Specific Condition No. 1 of Title V Permit No. 0180-00031-V1. This paragraph will remain effective until the permit action containing the use of the upstream NO_x CEMS and the method of calculating ammonia emissions is issued. The requirements of this paragraph are in addition to those specified in Title V Permit No. 0180-00031-V1, and do not relieve the Respondent from compliance with the requirements of Part 70 Specific Condition No. 1 or any other requirements of Title V Permit No. 0180-00031-V1.

Also, Respondent shall submit to the Enforcement Division, within thirty (30) days after issuance of the permit action, a notification that the requirements of the above paragraph have been achieved.

VI

Respondent further agrees that the Department may consider the inspection report(s), the Consolidated Compliance Order and Notice of Potential Penalty, and this Settlement for the purpose of determining compliance history in connection with any future enforcement or permitting action by the Department against Respondent, and in any such action Respondent shall be estopped from objecting to the above-referenced documents being considered as proving the violations alleged herein for the sole purpose of determining Respondent's compliance history. The consideration of such documents for the sole purpose of determining Respondent's compliance history and the estoppel pertaining thereto, do not negate or render null and void Respondent's denials herein of 1) any violations, including statutory and regulatory violations, and 2) any liability for any fines, forfeitures and/or penalties, and such denials are, and shall remain, in full force and effect in all respects.

VII

This agreement shall be considered a final order of the secretary for all purposes, including, but not limited to, enforcement under La. R.S. 30:2025(G)(2), and Respondent hereby waives any right to administrative or judicial review of the terms of this agreement, except such review as may be required for interpretation of this agreement in any action by the Department to enforce this agreement.

VIII

This settlement is being made in the interest of settling the state's claims and avoiding for both parties the expense and effort involved in litigation or an adjudicatory hearing. In agreeing to the compromise and settlement, the Department considered the factors for issuing civil penalties set forth in LSA- R. S. 30:2025(E) of the Act.

ΙX

The Respondent has caused a public notice advertisement to be placed in the official journal of the parish governing authority in Ascension Parish, Louisiana. The advertisement, in form, wording, and size approved by the Department, announced the availability of this settlement for public view and comment and the opportunity for a public hearing. Respondent has submitted a proof-of-publication affidavit to the Department and, as of the date this Settlement is executed on behalf of the Department, more than forty-five (45) days have elapsed since publication of the notice.

X

Payment in the form of a check, No. 204115, for \$3,357.95 was received by the Department on March 8, 2007, by the Office of Management and Finance, Financial Services Division, Department of Environmental Quality, Post Office Box 4303, Baton Rouge, Louisiana, 70821-4303.

XI

In consideration of the above, any claims for penalties are hereby compromised and settled in accordance with the terms of this Settlement.

XII

Each undersigned representative of the parties certifies that he or she is fully authorized to execute this Settlement Agreement on behalf of his or her respective party, and to legally bind such party to its terms and conditions.

PRAXAIR, INC.

	1 1/1/2/2
	BY: Jame Affected
	(Signature)
	Anne K. Roby, Ph.D.
	(Print)
	Vice President
	TITLE: <u>South Region</u> North American Ind'l Gases
THUS DONE AND SIGNED in dup	olicate original before me this <u>19th</u> day of , at <u>HOUSTON</u> , TEXAS
and the same of th	An Dimin
V. A. EDWARDS Notary Public, State of Taxas My Commission Enginee	NOTARY PUBLIC (ID #)
JULY 22, 2011	No mic Tobbie (ib #
	V. A. EDWARDS
	(Print)
	LOUISIANA DEPARTMENT OF
	ENVIRONMENTAL QUALITY
	Harold Leggett, Ph.D., Secretary
	Vanon 11 at
	BY: Oly M. WOOL
	Peggy M. Hatch, Assistant Secretary Office of Environmental Compliance
	office of Environmental Compitation
1	Znd
THUS PONE AND SIGNED in dur	plicate original before me this day of
	_, at Baton Rouge, Louisiana.
Q	Alb d
	1/0039
	NOTARY PUBATIO (ID # 1053)
	7 / PX / K. Droyle, The
, /	(Print)
$I \cap I \cap I$	/
	1 -
Approved: Cill Track	<u></u>
/Harold Leggett, Ph.D., Assistant	Secretary